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REMOVAL OF DYE FROM WASTEWATER OF TEXTILE INDUSTRY USING MEMBRANE TECHNOLOGY

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Abstract. Homemade textile industry is very famous in the East Coast of Peninsular Malaysia. Known locally as Batik Industries, they are traditionally inherited from generation to generation. The Batik Industry makes a big contribution to the economic growth due to high demands locally and from abroad. However, this industry produces wastewater which contributes to water pollution since it utilizes a lot of chemicals. Preliminary studies show that the wastewater from this homemade textile industries contains grease, wax, heavy metal, surfactant, suspended solid, and dyes (organic and inorganic). This paper explores the use of microfiltration membrane separation processes to remove the suspended solid (mainly due to dyes in the painting and coloring processes) from wastewater of batik industry. With the fabrication of a suitable experimental rig, the effect of dye concentration, dye pH, and operating pressure were studied. Data on the flux and rejection together with the average values for each of the parameters studied were presented systematically. The results show that the dye concentration, pH of dye, and the operating pressure was found to affect the filtration process. The average flux was reduced when the dye concentration was increased. The experimental results reveded that flux increased when the applied pressure was increased with the highest flux was observed at pH 4. The data collected could be used to improve the effectiveness of dye removal from the batik industry wastewater using membrane technology.

Keywords: Microfiltration, membrane separation, textile industries, batik, dyes

Abstrak. Industri pembuatan tekstil secara kecil-kecilan terkenal di pantai timur Semenanjung Malaysia. Ia dikenal oleh penduduk tempatan sebagai industri batik dan diwarisi secara turun-temurun. Industri batik banyak menyumbang kepada pembangunan ekonomi negara kerana sambutan yang menggalakkan bukan sahaja dari pasaran tempatan malah dari luar negara. Di sebalik perkembangan ini, industri batik turut menghasilkan air sisa yang mengakibatkan pencemaran air kerana prosesnya yang menggunakan bahan kimia yang banyak. Kajian awal terhadap air sisa industri batik menunjukkan bahawa ia mengandungi gris, minyak, logam berat, surfaktan, pepejal terampai, dan pewarna (organik dan tak organik). Permasalahan ini telah mendorong penyelidik mengkaji penggunaan proses membran bagi penurasan mikro untuk menyingkir bahan pepejal terampai (terutama yang dihasilkan oleh proses pengecatan dan pewarnaan) daripada air sisa industri batik. Dengan bantuan sebuah rig uji kaji yang sesuai, kesan kepekatan pewarna, pH suapan pewarna, dan tekanan operasi telah dikaji. Keputusan kajian menunjukkan bahawa kepekatan pewarna, pH suapan pewarna, dan tekanan operasi mempunyai kesan terhadap proses penapisan. Fluks purata didapati berkurang apabila kepekatan pewarna meningkat. Keputusan kajian menunjukkan bahawa fluks meningkat seiring dengan peningkatan tekanan dengan fluks tertinggi diperoleh pada pH 4. Data kajian boleh digunakan untuk meningkatkan keberkesanan penyingkiran pewarna yang terdapat dalam air sisa bagi industri batik dengan menggunakan teknologi membran.

Kata kunci: Penurasan mikro, pemisahan membran, industri tekstil, batik, pewarna

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1.0 INTRODUCTION

Homemade textile industry is very well known in Malaysia especially in the East Coast of Peninsular Malaysia and Sarawak. This industry is traditionally inherited from generation to generation. High skills coupled with the right equipments and tools are needed in order to produce batiks of high quality. Today, this industry has become very commercialized and contributed positively to the economic growth for some states such as Kelantan and Terengganu. Moreover, this industry has become the main attraction of foreign and local tourists to visit these states apart form other attractions such as an Islamic ruled government and many more [1]. Traditionally, the process of making a batik industry is shown in Figure 1.

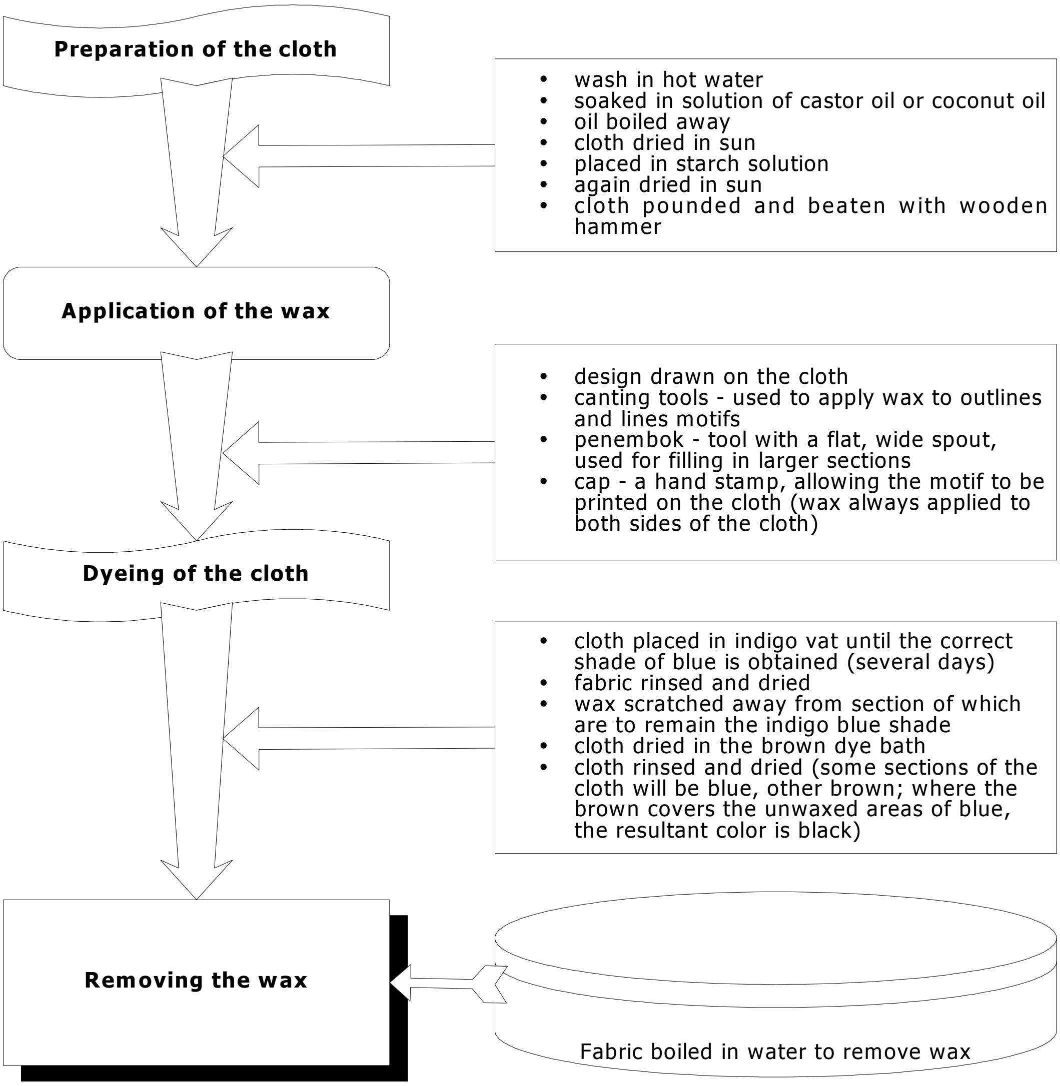

Figure 1 Schematic diagram of a batik process [15]

It is started from the preparation of cloth and raw materials and the use of suitable equipment until drying process. The process of batik painting starts with the preparation of fabrics, dyes, waxes, chemicals (ludigol, natrium silicate, sodium carbonate, sodium alginate, and potassium aluminum sulfate) and the equipment and tools which are the canting tool and stove. The painting process consumes large volume of water for washing. The process is continued with the application of wax on the fabric. Conventionally, the dye obtained from natural resources like plant and insect were used for batik textile.

Nowadays, dyeing process uses both organic and inorganic synthetic dye that available in variety of colours. It is first pulled through a chemical agent that helps the dye to bond to the cloth. The dye reacts with the chemical agent to produce the final colour. Chemical substance such as ludigol is added into dilute dye to get a brighter and more vibrant colour. Besides, alum (potassium aluminum sulfate) is used in fabric pretreatment process before marbling, so that the design can be applied well on the fabric. Sodium alginate is used to thicken the dye for screening, printing, painting or to control spreading [2]. In batik industry, nowadays, synthetic and/or chemical dyes are used widely. Most of the batik producers use reactive dye as the colouring substance and the plain fabrics are imported from China, India, and Japan. By using pencil and stencil, variety of design can be applied on the fabrics. It is normally done by the skilled designer who incharge of producing new and attractive design from time to time. The design and colour combination are very important to have a good market value. Usually the design is based on nature such as flowers, trees, and sceneries.

Canting process using simple tools; the canting and small thin wall spouted copper container that is connected to a short bamboo handle. The copper container is filled with melted wax to draw the design on clothes. Next the cloth is dyed. Again, it requires skills in order to produce a good combination of colours. Finally the decorated and painted fabrics is boiled. This process is very important to remove all the wax that protects the dye from spreading during the painting process. In this process, a lot of chemicals and suspended solids including dyes may be removed from the surface of the batik. Eventually the batik is dried under mild sun to protect the colours. Also, removing the wax consumes large volume of water.

The boiled water after the boiling process is normally discharge and can be considered as wastewater from the batik industry without further treatment. It produces a variety of waste streams that vary widely with respect to parameters such as grease surfactant contain, suspended solids and colours. Thus, it contributes water pollution due to the usage of many chemical substances.

1.1 Dyes

There are more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff produced annually. Due to their chemical structure, dyes are resistant to fading on exposure to light, water, and many chemicals [3]. Due to their complex structure and synthetic origin, many dyes are difficult to be decolorized and decomposed biologically. There are many structure varieties such as acidic, basic, disperse, azo, diazo, anthroquinone based, and metal complex dyes.

Azo dyes, for example, have the following of preparation by two basic reactions; diazotization and coupling. The reactions are:

$$R\text{-}NH_2 + 2HX + NaNO_2 \rightarrow RN_2^{+}X^{-} + NaX + 2H_2O \quad (1)$$

(diazonium salt)

$$R\text{-}N_2X + R'H \text{ ® } R\text{-}N{=}N\text{-}R' + HX \quad (2)$$

(azo dye)

where $X = Cl^-, Br^-, NO_3^-, HSO_4^-, BF_4^-$, and so on, and R = aryl group [4].

These dyes are very stable and decomposed only at temperature higher than 200°C. For this reason, synthetic dyes often receive considerable attention from researchers in textile wastewater treatment processes.

1.2 Methods of Treating Dye-containing Wastewater

Dye released to the waste stream, if without proper treatment, could exert great impact to the environment. Hence, for protecting the environment and to meet the stringent government law, many researchers try to find an effective and economical way of dye-containing wastewater treatment. Several studies have been performed on three categories. They are chemical, physical, and biological methods. Currently, the main methods of textile dye-containing wastewater treatment are physical and chemical means as shown in Table 1.

The oxidation agents used in practice or in research project (removal residual colour) are chlorine, or hydrogen peroxide and the later usually together with iron (II) sulfate (Fentons reagent), ozone, or UV irradiation. Heikkilal *et al.* [5] degraded some azo dye to decolorize using lignin peroxidase isoenzyme. They found that azo dye (certain) degraded to some extent and ability to degrade varied between lignin peroxidase isoenzymes and optimum pH for decolorization differed among dye. Lin and Liu [6] used combination of ozonation and coagulation for treatment textile wastewater. It is shown that ozonation effectively remove complete decolorization of textile wastewater in less than 10 minutes in the continuous reactor. Also, coagulation removed dissolved and suspended solids with a COD removal efficiency of up to 66%.

Even though dyes are difficult to be degraded biologically, many researchers interested in dye-containing wastewater. Buys and Renolds [7] have studied various kinds of dye wastewater using biological process. They found that COD and the colour of dye wastewater could not be efficiently removed. Bell *et al.* [8] treated and decolorized dye-wastewater using an anaerobic baffled reactor. It reduced in COD of 50 –

Table 1 Advantages of physical and chemical methods of dye removal from industrial effluent (Robinson, 2001)

Physical/chemical method	**Advantages**	**Disadvantages**
Fentons reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-product
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amine
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface area for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Remove all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Elektrokinetic coagulation	Economically feasible	High sludge production

60% and colours of about 95%. In addition, physical chemical processes, for example chemical coagulation, active-carbon adsorption, and ozone oxidation studies showed that the decrease of COD and colour for dye wastewater was not efficient. These above-mentioned processes could not completely treat the dye wastewater.

Lastly, flying ash was investigated [9] for its ability to absorb dyes from aqueous. Batch pH, kinetics and isotherm studies were performed in laboratory scale with synthetic dyes. Four concentrations of solution with different compositions and particles size were treated with fly ash (granular activated carbon) and the results exhibited reasonably good synthetic dye removal.

1.2.1 Membrane Process Application to Dye Removal for Textile Wastewater

A membrane is a permeable or semi-permeable phase, often known as a thin polymeric solid, which restricts the motion of certain species. Membrane, is a barrier that is to allow one component of mixture to permeate the membrane freely, while hindering permeation of other component. Membrane separation can be operated in two major modes that are the direction of feed stream to the orientation of membrane. They are known as dead end filtration and cross flow filtration [4,10].

Membrane separation process has the ability to clarify, concentrate and most importantly, to separate dye continuously from effluent [11,12]. Wu *et al.* [13] used membrane and combined with ozonation process for treatment of reactive-dye wastewater. Membrane separation process generated a permeate with over 99% of colour and copper removed. While 85 % of salt and 85% of the original water were reusable. Ciardelli *et al.* [14] combined activated sludge oxidation, sand filter, and ultrafiltration. The operation run at 8 bar pressure, and produced 60% of permeate from the inlet flow.

This research used dead-end microfiltration to remove dye-containing wastewater. Microfiltration membrane was chosen since the size of dye used was unknown. Bigger pore size of microfiltration membrane would enable to observe the effect of pore blockage as well as the cake formation of the dye which was smaller the pore size. The effect of some experimental parameters such as concentration of feed solution, pH of the feed, and pressure differences were carried out. The data and results were analyzed based on average flux and average rejection of dye particles. Through this experimental work, more understanding about the application of membrane and discussion about average flux rate, average percentage rejection, pore blocking, and membrane fouling would be presented. In order to carry out the experiment, an experimental rig was fabricated to study the effect of concentration or the effectiveness of recovery of dyes from batik industries. The rejection, R, could be calculated using the following expression where C_1 is feed concentration and C_2 is the permeate concentration.

$$R = \frac{C_1 - C_2}{C_1} \tag{3}$$

The results of this work would identify the optimum condition for this process.

2.0 EXPERIMENTAL PROCEDURE

A laboratory-scale filtration unit set up was designed and fabricated, which consisted of a feed tank, a centrifugal feed pump, valves, a filtration unit, and measuring equipment (pressure gauge meter, pH meter, analytical balance, stop watch, and turbidimeter). The filtration unit was a flat sheet, dead end filtration module. The overall process feed chamber were 11.2 cm × 3.4 cm × 0.3 cm, and the effective working area of the membrane was 23 cm^2. The membrane was supported on a stainless steel of 200 mm pore size, which was in turn supported a stainless steel mesh. Polyether cellulose membrane with 0.45 mm pore size was used (Millipore, Cat No. HAH00010). The schematic diagram of the whole experimental set up is shown in Figure 2. The

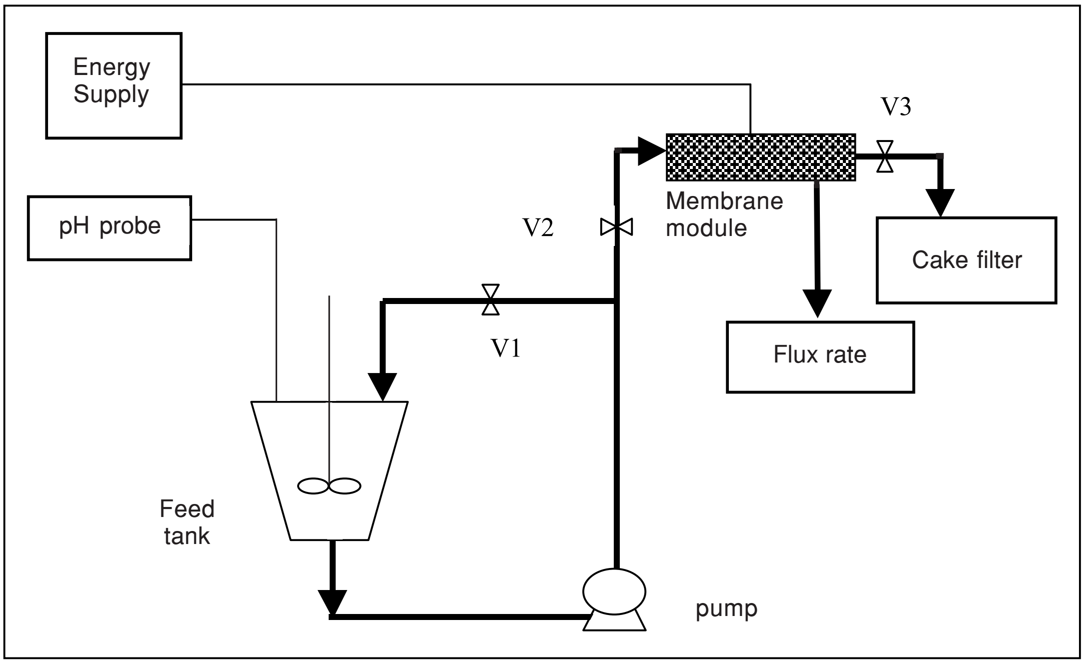

Figure 2 Schematic diagram of the experimental rig

valves V1 and V2 were adjusted to find the required pressure and to obtain the perfect mixing.

The dye, C.I. reactive blue, was obtained from Daystar Textifarben GmbH Co. The concentration of dye solution was prepared at 25°C and introduced at 10 kPa of pressure inlet membrane process. The pH process was adjusted to the required pH by adding dilute (0.1 M) NaOH or HCl. The experimen was operated at dead end mode and was run for two hours for each variable concentration. The flux was recorded by measuring the filtrate volume collected for every ten minutes. The average of 5 experimental reading were taken. The permeate was collected every ten minutes and its turbidity was measured using turbidimeter (HACH 2100). Their NTU reading from the turbidimeter was measured and compared to the calibration graph of known concentration (0.5; 1.0; 3.0; 5.0; 7.2; and 10.0 g/L) to calculate the actual concentration of the dye in permeate stream.

3.0 RESULTS AND DISCUSSION

3.1 Calibration Curve

Figure 3 shows the result for calibration curve. It clearly shows that the NTU reading is proportional to the concentration of the dyes. This calibration curve is used to determine the concentration of dye in the permeate solution collected from time to time through out the 2 hours experiment.

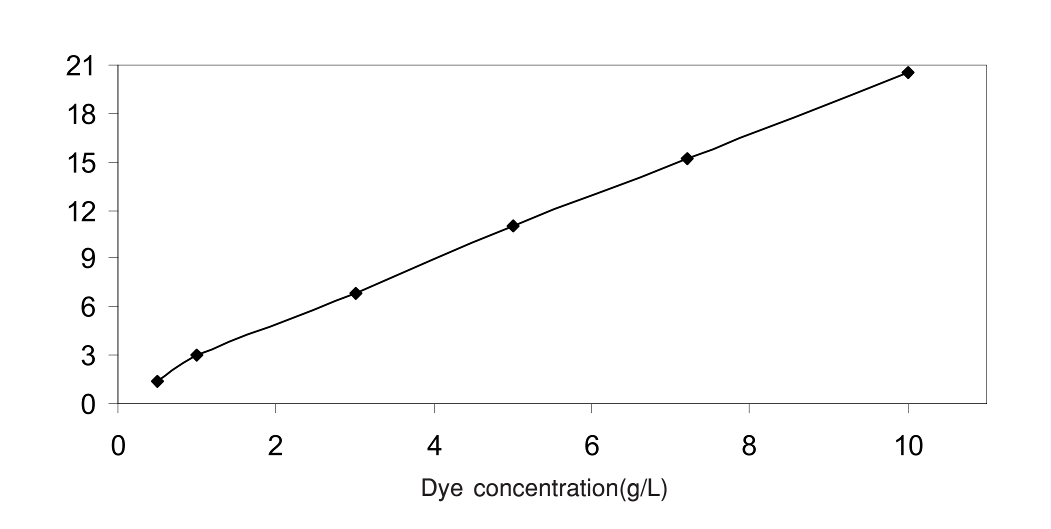

Figure 3 Calibration curve of C.I reactive blue 38

3.2 Effect of Dye Concentration

Table 2 shows the average flux and the average rejection for microfiltration recovery of dye at different feed concentrations. It clearly shows that when the feed concentration of dye increased from 0.5 to 10 g/L, the flux decreased tremendously from 1904 to 208 L/m^{2}h. This was due to the blockage membrane pore blocking and membrane fouling as the feed concentration increased, more dye particles would be collected on the surface of the membrane.

Table 2 Average flux and average rejection at different concentration of dye (@P = 2.0 kPa, pH=7)

Dye Concentration (g/L)	Average Flux (L/m^{2}h)	Average Rejection (%)
0.5	1904	21
1.0	391	30
5.0	235	85
10.0	208	91

On the other hand, the average percentage rejection increased as the feed concentration increased. At 0.5 g/L feed concentration, the average rejection was only 21% which means that more dye particles were penetrating through the membrane pores. As the feed concentration increased to 1 g/L, the average rejection increased to 30% which slightly higher than the earlier one. When the feed concentration increased to 5 g/L, the rejection increased tremendously to 85%. Further increment of the feed concentration to 10 g/L increased the average rejection to 91%. These results showed clearly that the membrane fouling at lower concentration was mainly due to the pore blockage. By increasing the feed concentration, the formation of cake on the membrane surface was found to be more dominant. These results also proved that the dye particle was smaller compared to the membrane's pore. This was clearly shown by the low average rejection, 21%, at the minimum cake formation when the feed concentration was 0.5 g/L.

Figure 4 shows how the flux varies against time at different feed concentration. Generally, the flux reduced with time. As explained above, at feed 0.5 g/L, the pore blockage was more dominant whereas for feed concentration of 1.0, 5.0, and 10.0 g/L, the formation of cake on the membrane surface was more dominant.

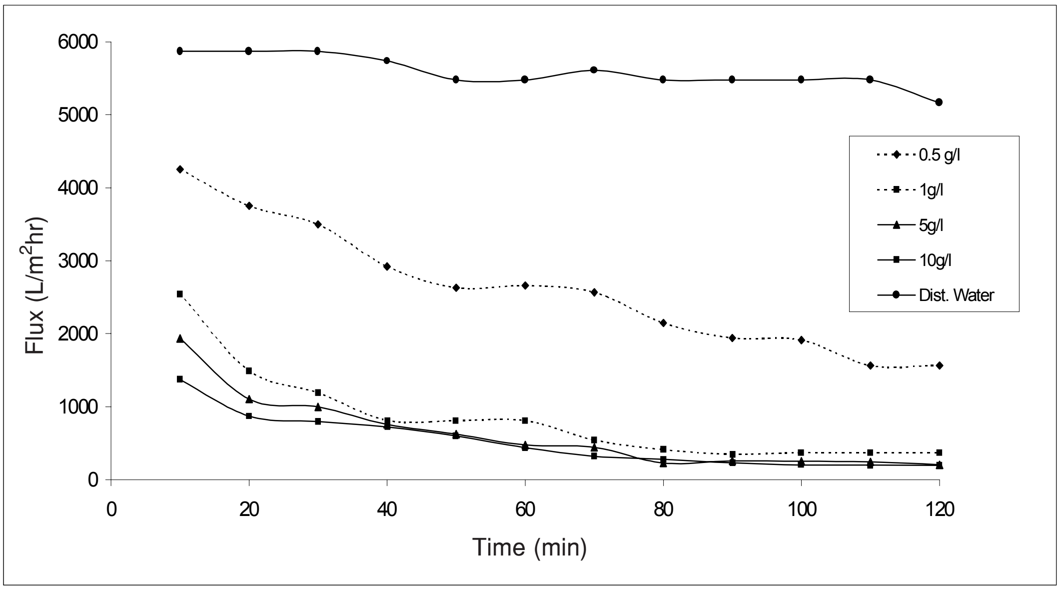

Figure 4 Flux at different concentration of dye vs time (@P = 2.0 kPa, pH=7)

Figure 5 shows more interesting pattern of rejection at different feed concentrations versus time. For 0.5 and 1.0 g/L feed concentration; starting at 6% and 20% respectively, the rejection only increased up to 38% and 50% each and their increment of rejection, @R were only 32% and 30% respectively. Whereas when the feed concentration was increased to 5 g/L, the increment of rejection was significant which starting from 40%, it increased to 90% after 2 hours (@R = 50%). Further increased of the feed concentration to 10 g/L gave very little increment of rejection. The rejection was 83% and end-up at 95% after 2 hours process which gave @R of only 12%. This concluded that even though the dye particle was smaller than the membrane pore size, but at high feed concentration, the average rejection was quite high, however the increment of rejection (@R) in 2 hours was very small (12 %). This was due to the faster formation of

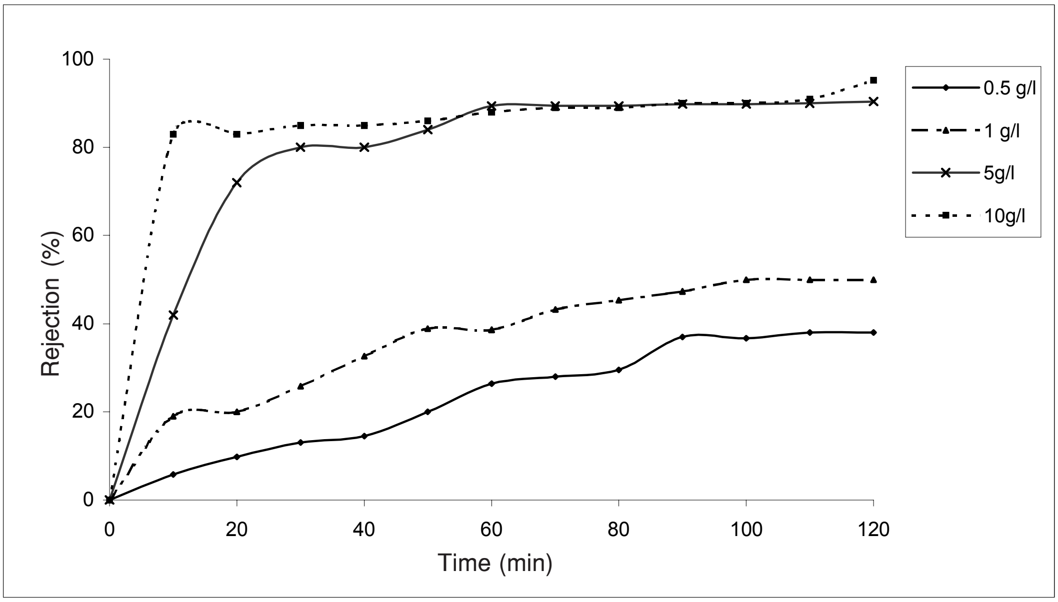

Figure 5 Rejection at different concentration of dye vs time (@P = 2.0 kPa, pH=7)

cake on the membrane surface right from the beginning of the process at high feed concentration.

3.3 Effect of dye pH

Table 3 shows the average flux and average rejection at different pH of the feed solution. Relatively, at pH 4, the flux was highest compared to the rest, because the mechanism for flocculation of dye particles was less at acidic solution. This smaller size of flocculate could penetrate easily. The average rejections were found to be close to each other. The highest value of rejection was 86% at pH 7. For variation of pH from pH 4 to pH 10, the higher flux was followed by the lower rejection. Similar trend was found for the effect of feed concentration as shown in Table 2.

From Figure 6, it is observed that there was slight difference in flux between different pH. The influence of acid or base in pH study showed the same pattern of flux against time.

Table 3 Average flux and average rejection at different dye pH (DP = 5.0 kPa, concentration=5 g/l)

Dye pH	Average Flux (L/m^2h)	Average Rejection (%)
4	414.22	75.0
6	328.56	82.4
7	300.68	86.0
8	376.59	80.0
10	369.96	78.5

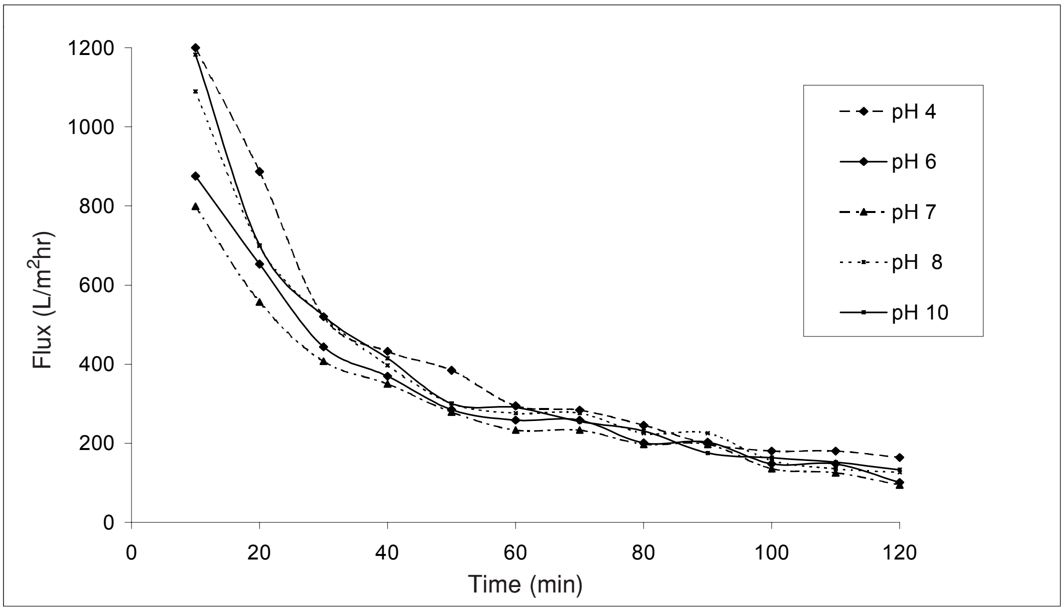

Figure 6 Flux at different pH of dye vs time (@P=5 kPa, concentration=5g/l)

Figure 7 shows how the percentage of rejection varies with time for different pH. From Figure 7, for the variation of pH from pH 4 to pH 10, the rejection at different pH value of feed were quite similar. The rejections increased extremely in the first 30 minutes

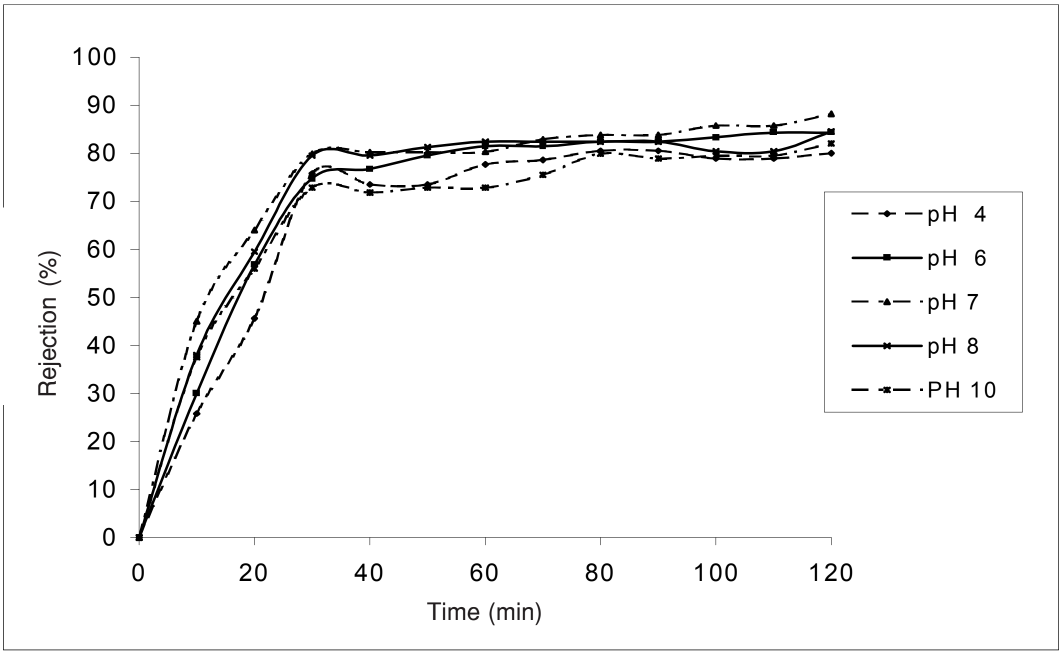

Figure 7 Rejection at different pH of dye vs time (@P=5 kPa, concentration=5g/l)

after a period of time (30 minutes) increased the resistance for dye to pass through the membrane and the pore blockage and cake formation became stable after 50 minutes. The highest rejection occurred at neutral pH and the lowest was at pH 10, because at neutral pH, the dyes particles were found to flocculate and formed the cake layer.

3.4 Effect of operating pressure

Based on Table 4, it could be concluded that the average flux increased when the applied pressure was increased. Also, the average percentage of rejection would be lower as the pressure increased as stated in any membrane separation theory.

Table 4 Average flux and average rejection at different operating pressure (pH=7, concentration=1g/l)

Pressure (kPa)	Average Flux (L/m^{2}h)	Average Rejection (%)
3.0	453.28	62.4
5.0	629.12	53.0
7.0	728.32	48.0
10.0	838.91	32.0

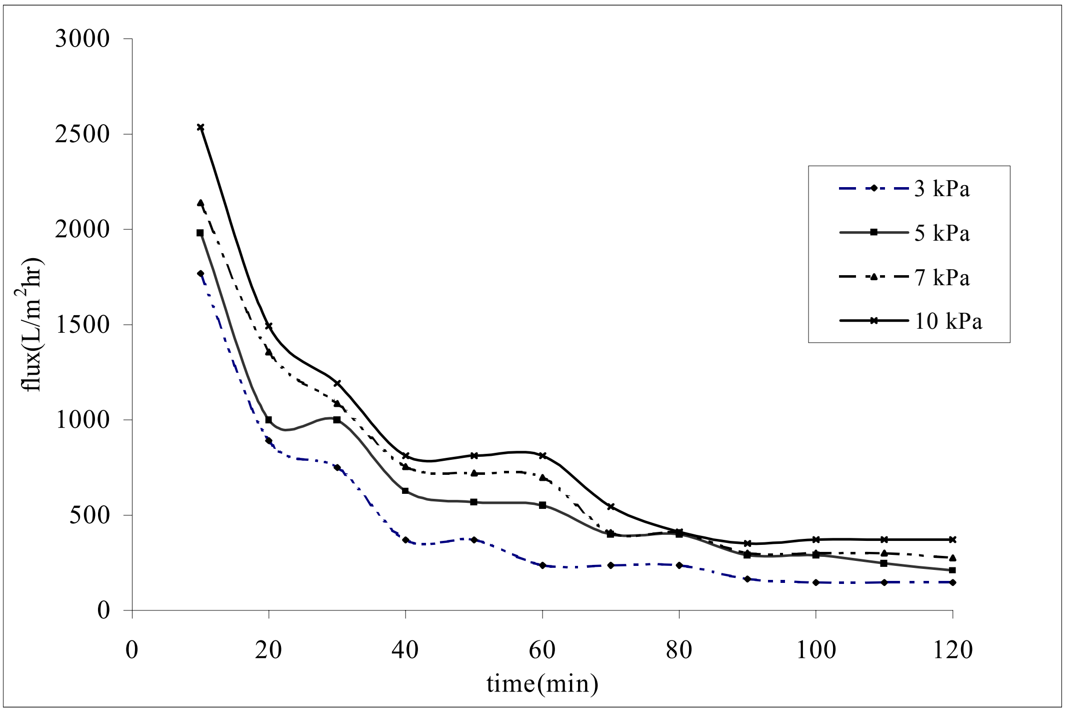

Figure 8 Flux at different operating pressure vs time (Concentration=1g/l, pH=7)

Figure 8 shows that the flux was at its highest at 10 kPa pressure, followed by 7 kPa, and 5 kPa and the lowest at 3 kPa. Thus, it could be concluded that the flux increased when the applied pressure was increased.

Figure 9 shows an interesting pattern of rejection. It was observed that the highest rejection percentage was at the operating pressure of 3 kPa. It started with 61% and the rejection ended up at 72% (DR = 11%). The increment of percentage rejection of 5kPa started with 45% and ended up at 68% (DR = 23%) after operating for two hours. For 7 kPa and 10 kPa , it started at 32% and 23% respectively, and the rejection increased up to 56% and 51% respectively. Overall, it was reasonable to conclude that the higher the pressure difference, the higher would be the driving force which pushed the particles through the membrane pore. Thus, the formation of cake on the membrane surface would be minimized and lowered the percentage of rejection.

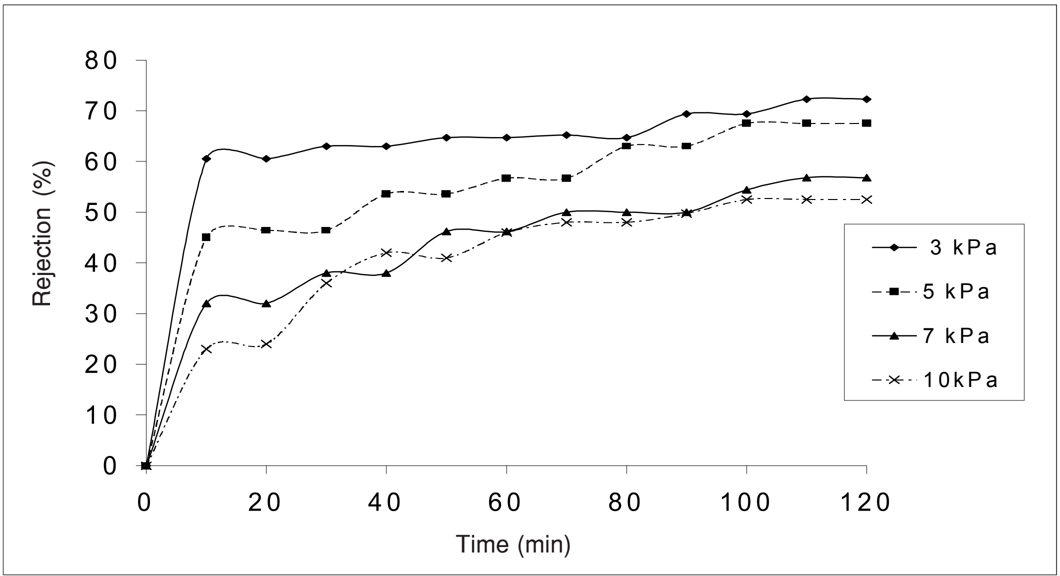

Figure 9 Rejection at different operating pressure vs time (Concentration=1g/l, pH=7)

4.0 CONCLUSION

The removal of dye from the wastewater of the batik industry was found to be feasible with the developed lab scale process. The dye concentration, pH of dye, and the operating pressure were found to have an effect on the filtration process. The average flux reduced when the dye concentration increased. The highest flux was observed at pH 4 and the flux increased when the applied pressure increased. At low feed concentration, pore blockage contributed to the membrane fouling. On other hand, at higher feed concentration, cake formation on the membrane surface was found to be more dominant and contributed to membrane fouling. This preliminary research showed that the microfiltration membrane has the potential to remove dye from the wastewater produced by the textile industry. More studies are required prior to employing this technology commercialy in the textile industry.

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